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ABSORPTION COEFFICIENT MEASUREMENTS
OF CO2 HDO-N2, AND CH4-AIR USING A DF
LASER

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Ohio State University

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|---|---|---|
| Molecular absorption | $CO_2$ carbon dioxide | Atmospheric absorption |
| Laser Propagation | HDO heavy water | |
| DF laser | Water vapor | |
| DF | Molecular Spectroscopy | |
| $CH_4$ methane | Atmosphere | |

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report presents measurements of the absorption of HDO-$N_2$ mixtures when illuminated with a DF laser operating on the 3-2 P(6) to P(8) lines. Similar data is presented for pure $CO_2$ and the 2-1 P(8) DF line. Measurements of $CH_4$-Air mixtures are presented for the 2-1 P(6) - P(8) DF lines.

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# ABSORPTION COEFFICIENT MEASUREMENTS OF $CO_2$ HDO-$N_2$, AND $CH_4$-AIR USING A DF LASER

F. S. Mills
R. K. Long

## FOREWORD

This report, Ohio State University Research Foundation Report Number 3271-10 (Tenth Quarterly Report), was prepared by The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering, Columbus, Ohio. Research was conducted under Contract F30602-72-C-0016, Job Order 12790502. Mr. James W. Cusack, RADC (OCSE), of Rome Air Development Center, Griffiss Air Force Base, New York is the Project Engineer.

This report has been reviewed by the RADC Information Office (OI), and is releasable to the National Technical Information Service (NTIS).

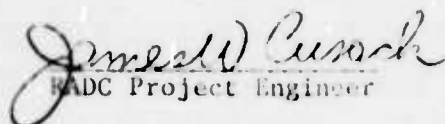This technical report has been reviewed and is approved.

*James W. Cusack*
RADC Project Engineer

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# I.  INTRODUCTION

Contributions to the molecular absorption coefficient for DF lasers arise from absorption by $N_2O$, $CH_4$, $CO_2$, HDO, and a water continuum.

Report RADC-TR-73-389[1] gave calculated values for the absorption coefficient for each of the above components. Since issuance of that report the following additional information has come to our attention.

According to Professor Benedict[2] the $CH_4$ calculations from the AFCRL data tape may be less accurate than the other coefficients in the $3.8\mu$ wavelength region.

Dr. Orlo Myers[3] has looked at $CO_2$ absorption experimentally and has found that the absorption coefficient in some cases is four orders of magnitude higher than shown in TR-73-389. We have also measured the $CO_2$ coefficient for the 2-1 $P(\mathcal{E})$ line and have confirmed this result. Our data is included with this report. The reason for the discrepancy, apparently, is that an isotopic $CO_2$ band exists in this region which was not included in the AFCRL data tape. The $CO_2$ coefficient is of the order of $10^{-4}$ $km^{-1}$ and therefore is still small compared to the water vapor coefficient at sea level.

Experimental results were given in a recent report[4] for five DF lines where $N_2O$ absorption was considered important.

Since the water coefficients are quite small their accurate measurement is difficult. In the case of the HDO component we have enhanced the absorption by using an enriched gas mixture (6.2 parts HDO to 100 parts total water) in the multi-path cell. The first data from these experiments is given in this report. It will be seen that the data scatter in these experiments is already very small.

Future work will include a more complete study of the limitations involved in extrapolation of the results of these experiments to normal atmospheric conditions; extension to more DF lines; and more careful analysis of the gas composition of the mixture.

Burch[5] studied the $3.8\mu$ water continuum by measuring the absorption of high pressure samples of pure water in an elevated temperature long path cell. It was then necessary to assume a broadening coefficient and to extrapolate temperature in order to estimate the coefficient for normal atmospheres. This was the method used in the calculations of TR-73-389.

We present here the derivation of formulas which will make easier the comparison of Burch's results with our experimental coefficients in $km^{-1}$. Burch[6] has pointed out that whether the continuum arises from line wings, pressure induced bands, or dimers the pressure dependence is the same, i.e., the absorption coefficient is proportional to pressure.

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Thus we can write

$$(1) \qquad T = e^{-[C_s\, e/760 + C_b\, P'/760]u} = e^{-k \cdot l}$$

where

$C_s$ = self-broadening coefficient $(\text{mol}^{-1}\text{cm}^2\text{atm}^{-1})$

$C_b$ = foreign broadening coefficient

$e$ = water vapor pressure in torr

$P$ = total pressure in torr

$P'$ = broadener pressure in torr = $(P-e)$

$u$ = water content of sample $(\text{mol cm}^{-2})$

$T$ = transmittance

$k$ = absorption coefficient $(\text{km}^{-1})$.

The water content of a one km path is given by

$$(2) \qquad u = .734 \times 10^{22}\, (e/760\,T) \times 10^5 \text{ mol cm}^{-2}$$

where $T$ is now temperature in deg K.

Now assume $C_b/C_s = .12$ [5] and combine equations (1) and (2) leading to,

$$(3) \qquad k = 1.53 \times 10^{20} \frac{C_s\, e}{T} [7.3\, e + P] \quad \text{km}^{-1}.$$

This formula used with the extrapolated Burch data[5] for 296 K will yield the values in report RADC-TR-73-389. We intend to state the results of our planned spectrophone experiments in terms of $C_s$ so that an easy comparison with previous work will be possible.

The experiments referred to will be performed using a spectrophone illuminated with a DF laser and using water vapor-nitrogen mixtures at ambient temperature. The laser is located at UARL in Hartford, Connecticut.

Calculated results are given in report RADC-TR-73-389 for 30 DF laser lines. Although most of these lines may eventually be studied experimentally, the present phase of the work is concentrated on a smaller number of lines.

For HDO we are studying,

| | |
|---|---|
| 3-2 | P(6), P(7), P(8) |
| 2-1 | P(6), P(7), P(8) |
| 1-0 | P(11) |

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and for $N_2O$,

$$3\text{-}2 \quad P(6), P(7), P(8)$$
$$2\text{-}1 \quad P(10), P(11).$$

## II.  HDO MEASUREMENTS

The equipment and data recording procedures for these experiments were identical to those described for the $N_2O$ measurements[4] and hence the description will not be repeated.

We are labeling the HDO data preliminary at this time since these measurements were performed using the same detector linearity corrections as were used with the $N_2O$ measurements.

Further detector calibration work is required for two reasons.  First there is the possibility of detector and or electronic circuitry changes with time of the order of months since the last calibration.  Second the laser power output is in general much higher for 2-1 lines than for 3-2 lines thus requiring a calibration over different detector voltage ranges.

In these experiments it was necessary to devise a careful sample preparation procedure.

In the steady state, HDO does not exist alone but rather in equilibrium with $H_2O$ and $D_2O$ according to the following equation:

$$(4) \qquad H_2O + D_2O \rightleftharpoons 2HDO.$$
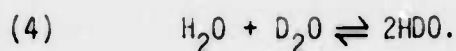
The relative concentrations of the three types of water can be calculated from the equilibrium constants, $K_{293^\circ} = 3.543$ and $K_{293^\circ} = 3.506$[7] for the liquid and gas phases respectively.

The procedure used in preparing the samples for the work presented here was to mix a known amount of $D_2O$ with a known amount of $H_2O$ and calculate the resulting amount of HDO using the equilibrium constant. A formula relating the final amount of HDO to the initial amounts of $D_2O$ and $H_2O$ can be derived as follows:

Let $C_{H_2O}$ be the initial volume of $H_2O$, $C_{D_2O}$ be the initial volume of $D_2O$, and $C_{HDO}$ be the final volume of HDO.  Using these definitions Eq. (4) becomes

$$(5) \qquad (C_{H_2O} - C_{HDO}/2)\, H_2O + (C_{D_2O} - C_{HDO}/2)\, D_2O \rightleftharpoons C_{HDO}\, HDO.$$

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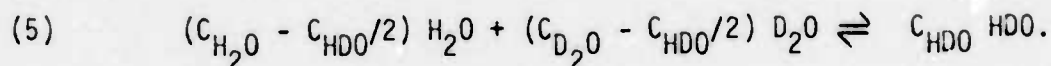
The terms in parentheses in Eq. (5), $(C_{H_2O} - C_{HDO}/2)$ and $(C_{D_2O} - C_{HDO}/2)$ are the final amounts of $H_2O$ and $D_2O$ respectively. The final amounts of $H_2O$, $D_2O$ and HDO are related to the appropriate equilibrium constant K by

(6)
$$\frac{(C_{HDO})^2}{(C_{H_2O} - C_{HDO}/2)(C_{D_2O} - C_{HDO}/2)} = K$$

or

(7)
$$\frac{(C_{HDO})^2}{C_{H_2O} C_{D_2O} - \frac{C_{HDO}}{2} (C_{H_2O} + C_{D_2O}) + \frac{(C_{HDO})^2}{4}} = K.$$

Equation (7) may be written as follows.

(8)
$$(C_{HDO})^2 (4-K) + 2K C_{HDO} (C_{H_2O} + C_{D_2O}) - 4K C_{H_2O} C_{D_2O} = 0.$$

Equation (8) may now be solved for $C_{HDO}$ using the quadratic formula.

(9)
$$C_{HDO} = \frac{-K(C_{H_2O}+C_{D_2O}) + \sqrt{K^2(C_{H_2O}+C_{D_2O})^2 + 4K(4-K)C_{H_2O}C_{D_2O}}}{(4-K)}.$$

For the measurements reported here the enhanced HDO mixture was prepared by mixing 10 ml. $D_2O$ with 300 ml. $H_2O$. This results in a mixture of liquid water containing 0.116% $D_2O$ and 6.219% HDO with the remainder being $H_2O$, or a gaseous mixture containing 0.118% $D_2O$ and 6.216% HDO with the remainder being $H_2O$. The concentration of HDO was taken to be 6.22 since the original amounts of $D_2O$ and $H_2O$ could not be measured accurately enough to justify carrying the third decimal place. The absorption due to $D_2O$ was not measured separately so there may be a small contribution to the absorption coefficients reported here which is caused by $D_2O$ as well as HDO.

In spite of the fact that the sample is approximately 94% $H_2O$ one can assume that the water continuum absorption in a one km path is so small that it will not cause an appreciable error in the measured HDO coefficients[1].

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There is another potential problem which could be encountered when the enhanced sample is introduced into the White cell. This is caused by the fact that HDO is less volatile than $H_2O$ and therefore remains preferentially in the condensed phase. It has been reported[8] that in thermodynamic equilibrium water vapor over liquid water will contain 8% fewer HDO molecules than the liquid water. When the water vapor is being introduced into the White cell, the liquid and gas are certainly not in thermodynamic equilibrium so the HDO concentration could be quite uncertain. This problem was overcome by filling a small bottle with just enough of the enhanced water to fill the White cell with the desired amount of water vapor and evaporating the sample completely.

One other problem which might possibly affect the HDO concentration would be preferential adsorption of HDO by the walls of the White cell. The cell has been tested several times for $H_2O$ adsorption and none has been detected. However this test has not been made with HDO. It is our intention to sample some enhanced water vapor-nitrogen mixtures and send them to a commercial laboratory for mass spectrographic analysis. Pending that analysis it is our belief that preferential HDO adsorption is not a problem.

We are also adding a mass spectrometer analyzer to our White cell so that the HDO/$H_2O$ ratio can be monitored as a function of time in order to evaluate some of the above potential problems. We do not expect that our instrument will be accurate enough for absolute concentration determinations. For that we intend to rely on the equilibrium constant method and the commercial laboratory analysis.

Figures 1, 2 and 3 show the results for the 3-2 P(6), P(7) and P(8) lines respectively. The absorption cell path length was 731.7 meters and originally contained 15 torr of the 6.22 parts HDO to 100 parts total water mixture plus nitrogen to a total pressure of 760 torr. The lower points on the curve were then obtained by partial pumpout of the sample followed by a refill to 760 torr with nitrogen.

For each line a least squares fit of the data to an expression of the form $K = Ap + Bp^2$ was made, where K is the absorption coefficient and p is the partial pressure of enriched water vapor in torr. The derived expression is presumed to be a more accurate characterization of the absorption coefficient than any individual data point. The expressions for the measured absorption coefficients for the three lines are presented in column 3 of Table I. The expressions are valid for 760 torr total pressure with p being the partial pressure of the enriched water. The absorption coefficients extrapolated to .03% HDO and 14.26 torr water vapor are presented in column 4 of Table II. These coefficients were obtained by evaluating the expressions in column 3 for p = 14.26 torr and multiplying by .03/6.22. This procedure assumes that line broadening caused by HDO - HDO collisions is about the same as line broadening due to HDO - $H_2O$
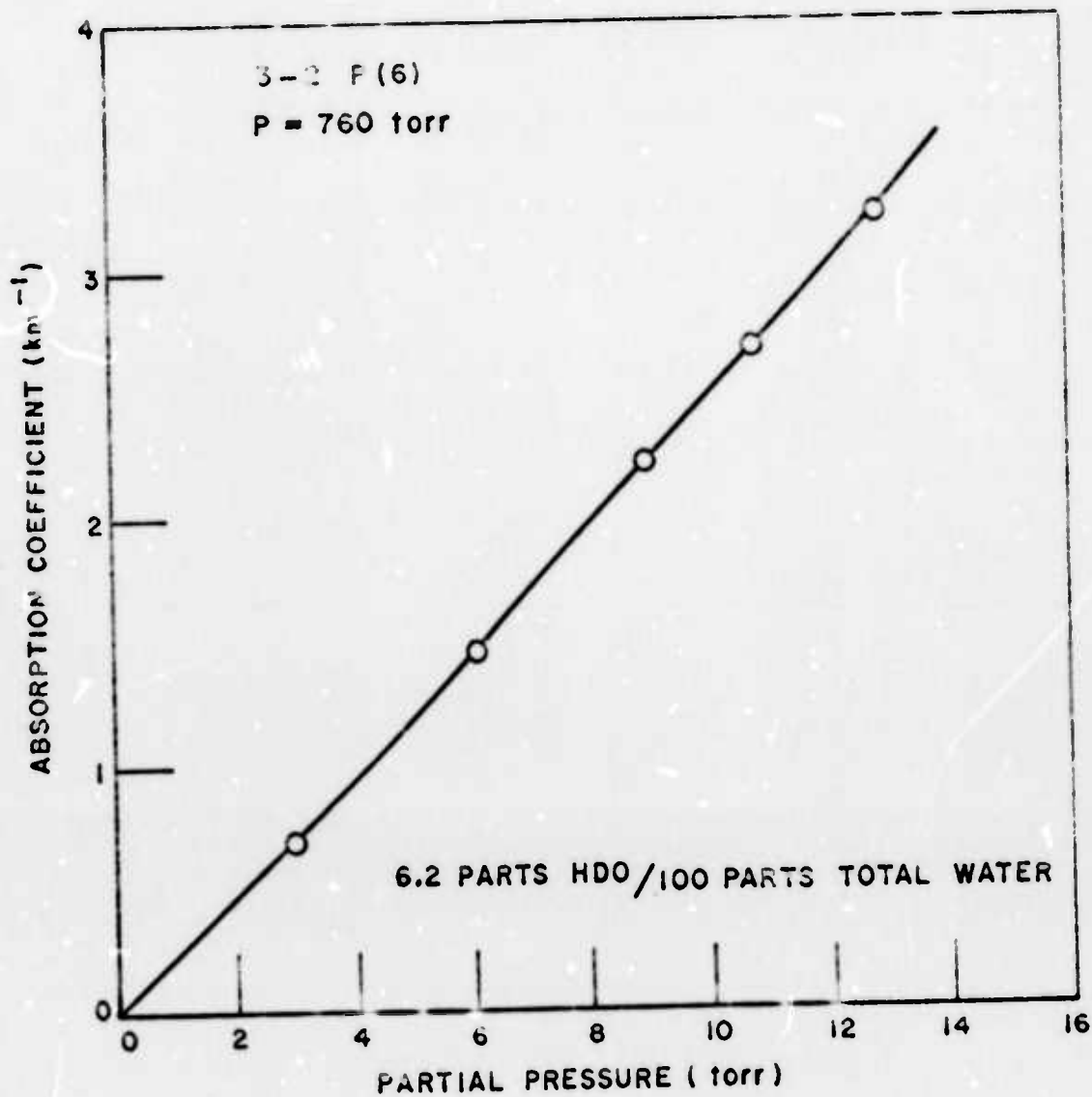
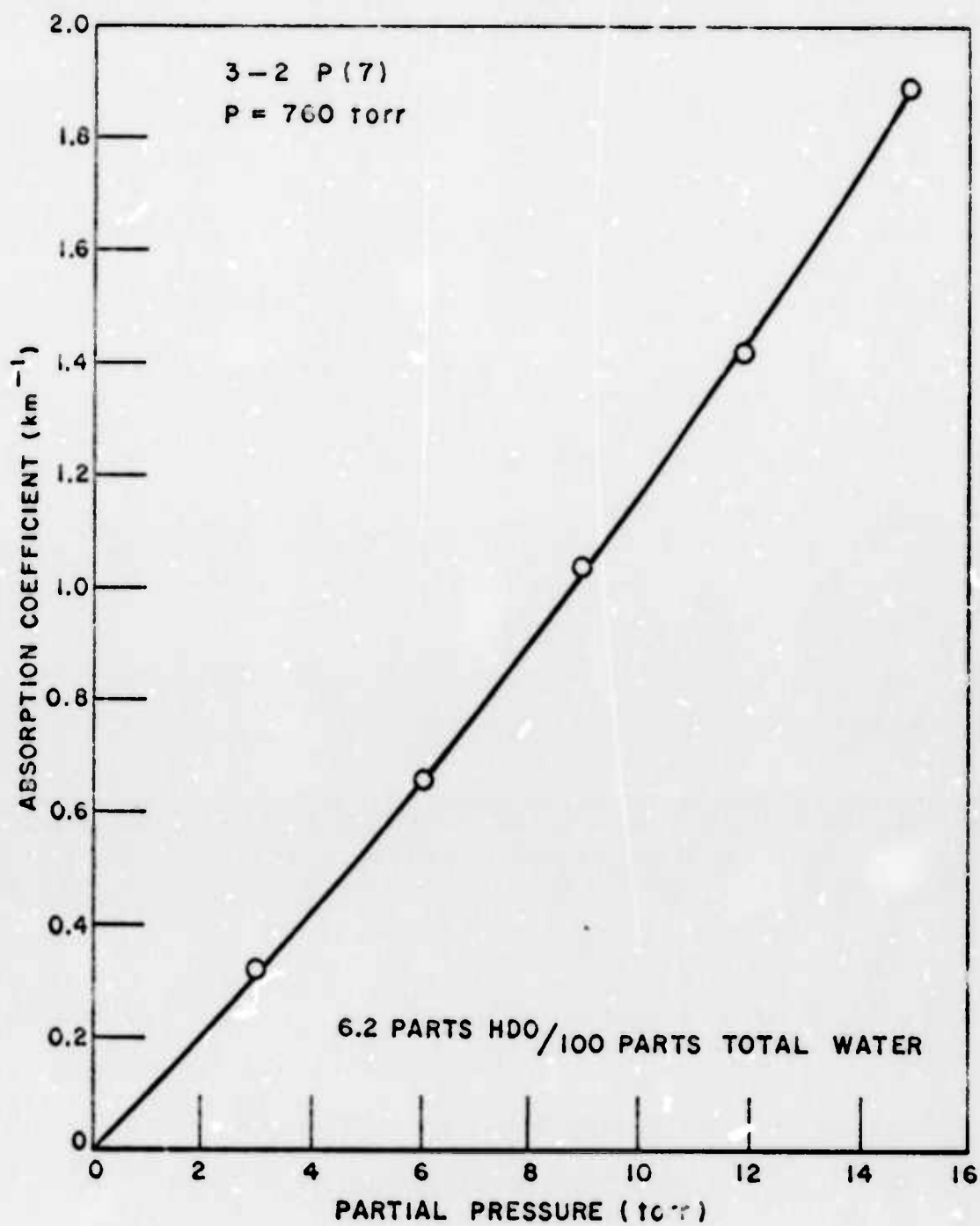Fig. 1. Measured HDO-N$_2$ absorption coefficient for 3-2 P(6) line.

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Fig. 2.  Measured HDO-N$_2$ absorption coefficient for 3-2 P(7) line.
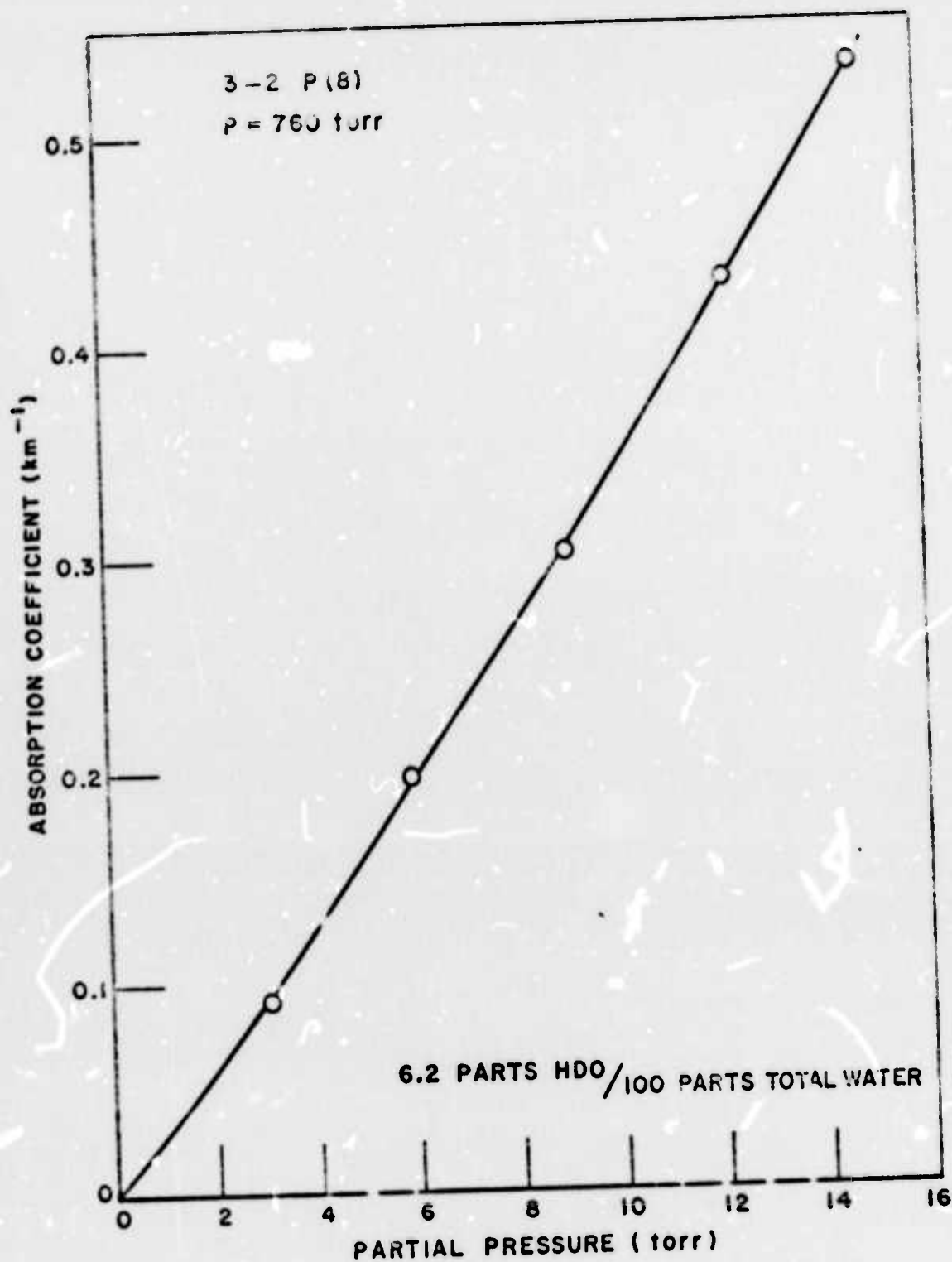
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Fig. 3. Measured HDO-N₂ absorption coefficient for 3-2 P(8) line.

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collisions. The absorption coefficients calculated from the AFCRL tape for 14.26 torr water and 760 torr total pressure[1] are presented in column 5 for comparison.

TABLE I

| Col. 1 | Col. 2 | Col. 3 | Col. 4 | Col. 5 |
|--------|--------|--------|--------|--------|
| Iden | $V$ $cm^{-1}$ | $K_{exp}$ at 0.22% HDO ($km^{-1}$) | $K^{OSU}$ .03%HDO, 14.26 torr $H_2O$ ($km^{-1}$) | $K_{calc}$ ($km^{-1}$) |
| 3-2 P(6) | 2594.25 | $.231p + 1.58 \times 10^{-3}p^2$ | .0174 | .00667 |
| 3-2 P(7) | 2570.51 | $9.77 \times 10^{-2}p + 1.93 \times 10^{-3}p^2$ | .00861 | .00478 |
| 3-2 P(8) | 2546.42 | $3.00 \times 10^{-2}p + 4.01 \times 10^{-4}p^2$ | .00246 | .00135 |

## III. PURE $CO_2$ ABSORPTION

Absorption of the 2-1 P(3) DF laser line at 2631.06 $cm^{-1}$ by pure $CO_2$ was measured for $CO_2$ pressure of 248, 503, and 761 torr in a path of 731.7 meters. The result of that measurement is shown in Fig. 4. The results of this experiment are less reliable than the HDO measurements because the detector calibration was not sufficiently well known. The point at 761 torr is probably within 10% with the other two points being somewhat worse. The measured absorption coefficient was 1.6 $km^{-1}$ at 761 torr. Assuming a broadening coefficient of 1 this corresponds to 5.3 x $10^{-4}$ $km^{-1}$ at 330 ppm $CO_2$ and 1 atmosphere total pressure. As discussed in the introduction this is higher than one computes from the AFCRL data tape[1] because the necessary $CO_2$ line data is not included in the tabulation.

## IV. $CH_4$ - AIR ABSORPTION

Absorption of the 2-1 P(6), 2-1 P(7), and 2-1 P(8) DF Laser lines by methane-air mixtures was also measured. The absorption cell was set for a path length of 731.7 meters and originally contained 2263 parts per million methane plus dry air to a total pressure of 760 torr. Lower concentrations were then obtained by partially evacuating the cell and refilling to 760 torr with dry air.
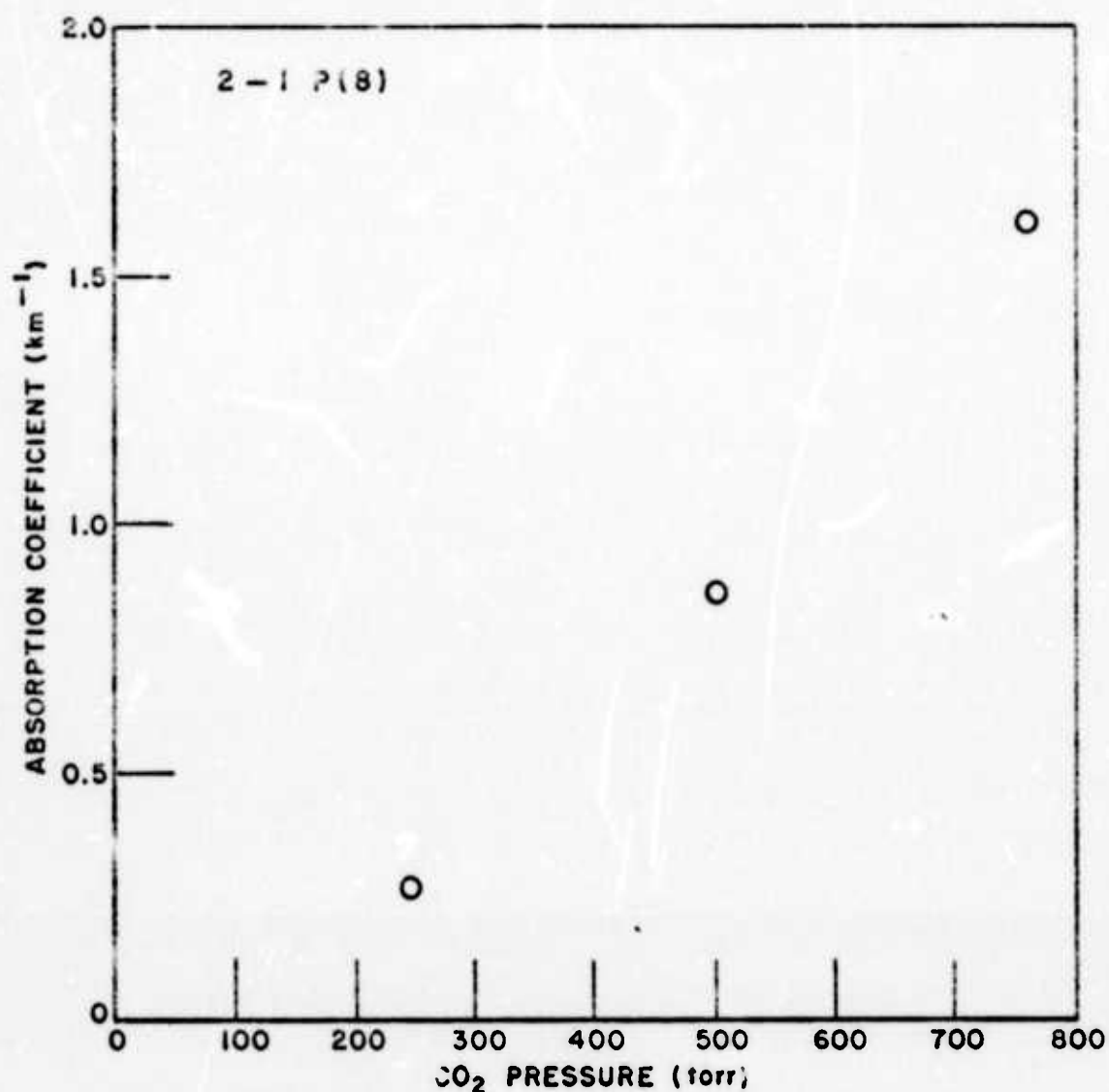
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Fig. 4.  Measured $CO_2$ absorption coefficient
for 2-1 P(8) line.

Before these measurements were made the detectors were calibrated
for the 2-1 band using the 2-1 P(10) DF laser line.  The equipment and
calibration procedure used were identical to those for the 3-2 band
calibration reported earlier[4] and will therefore not be repeated.

Figures 5, 6, and 7 show the measured absorption coefficients
versus $CH_4$ concentration for the 2-1 P(6), P(7), and P(8) lines respectively.
For each line, a least squares fit of the data to a straight line through
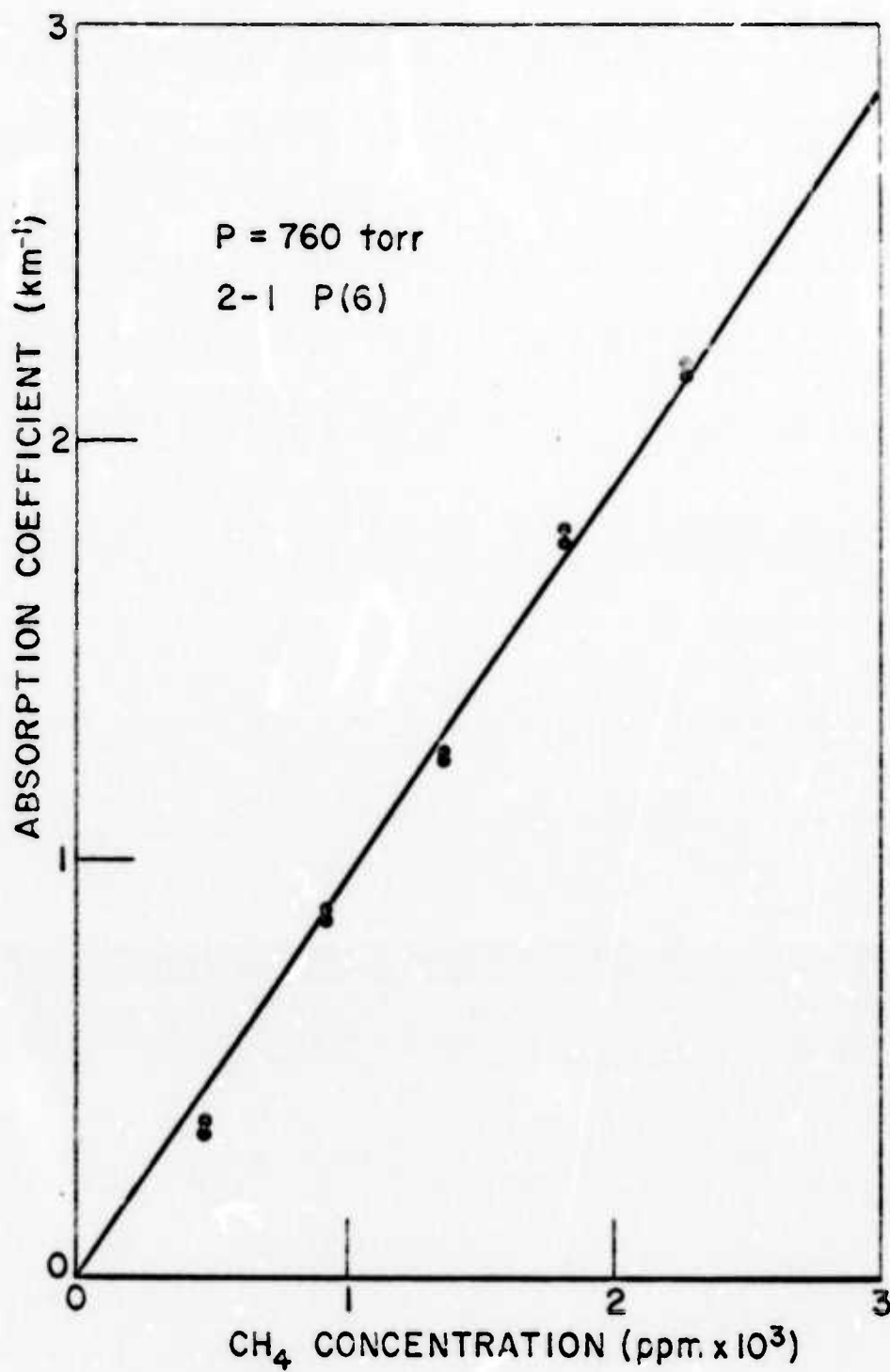the origin was made.

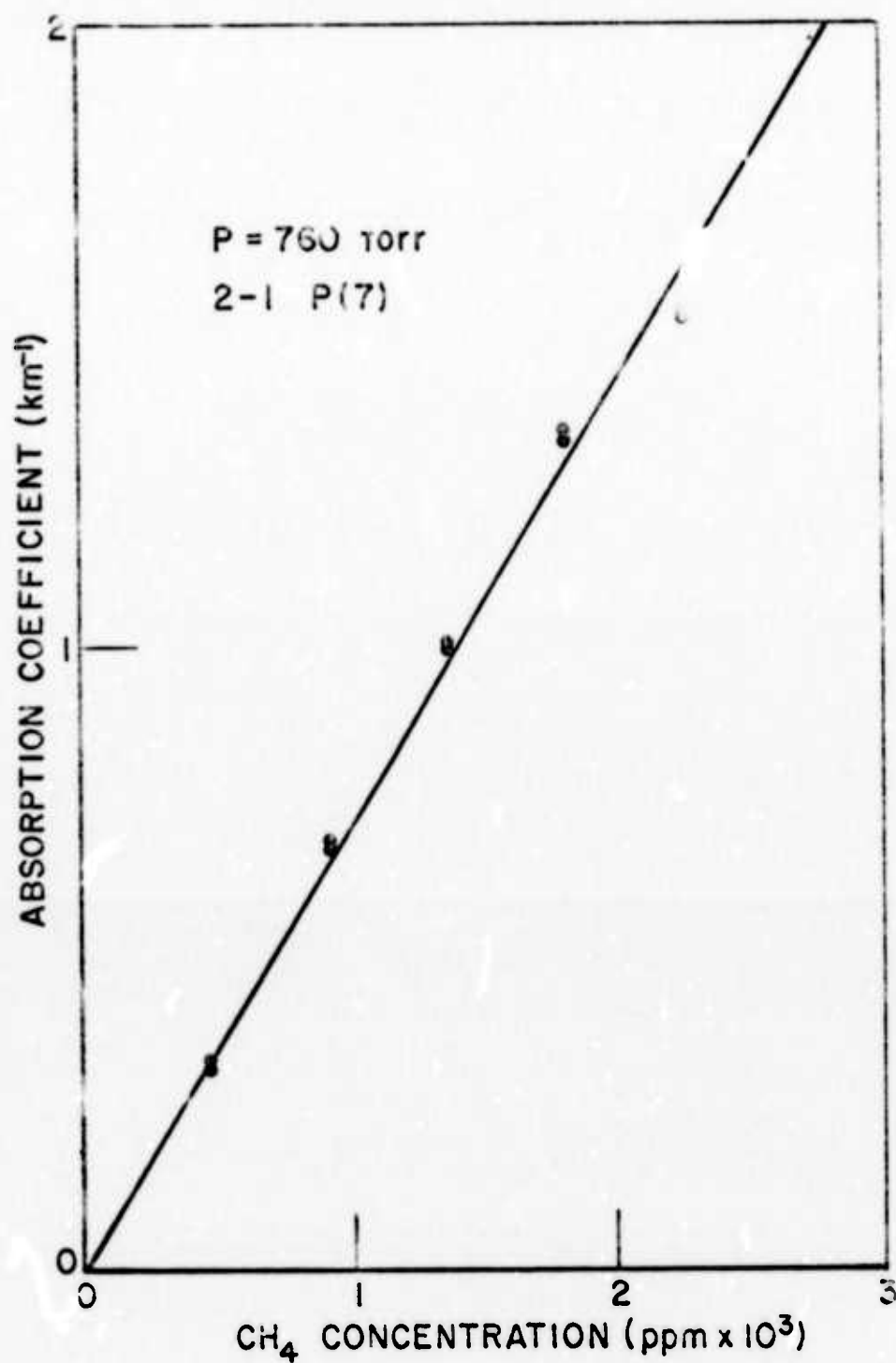Fig. 5.    Measured $CH_4$ - Air absorption coefficient for 2-1 P(6) line.

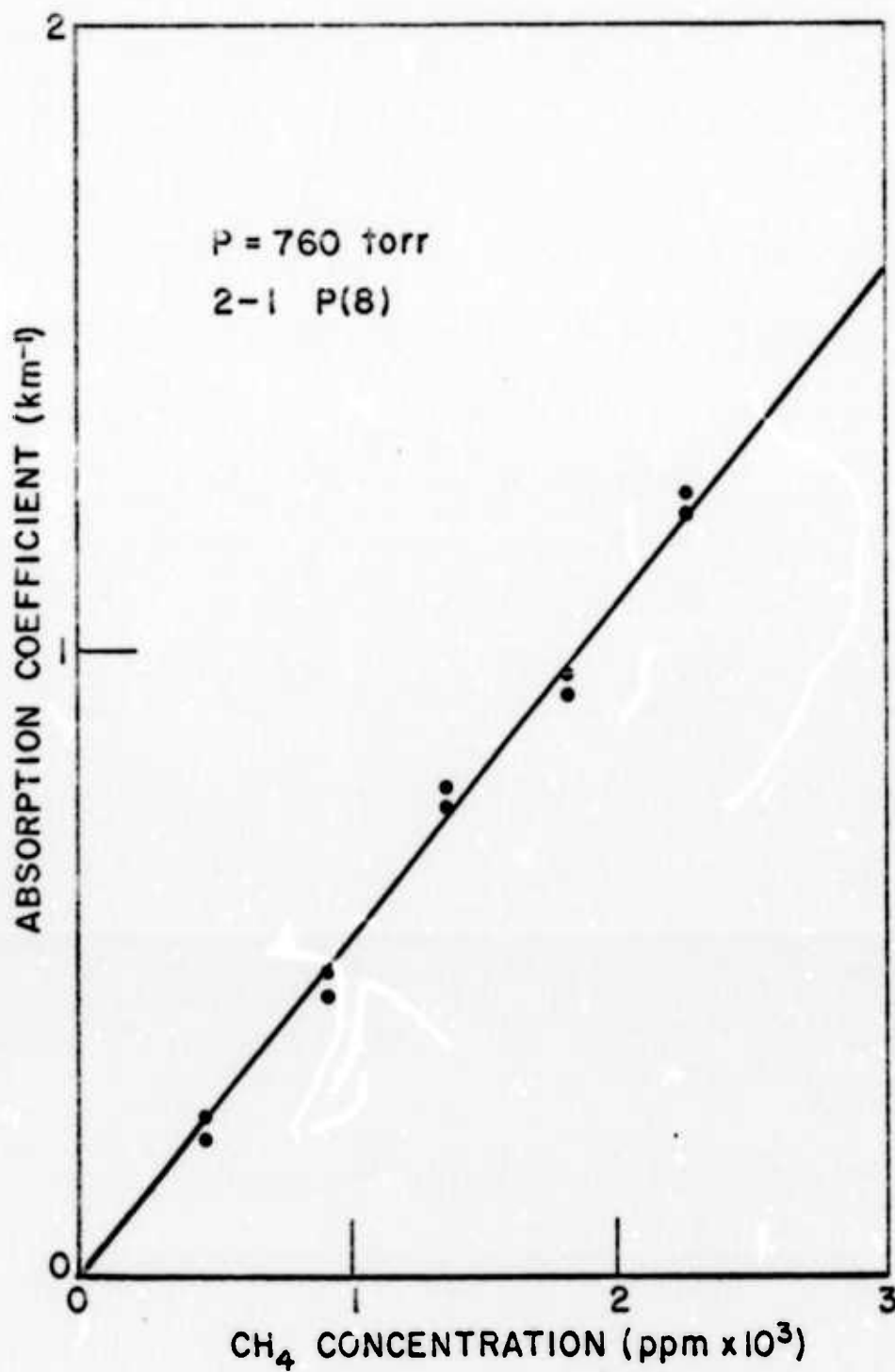Fig. 6. Measured CH₄ - Air absorption coefficient for 2-1 P(7) line.

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Fig. 7. Measured CH₄ - Air absorption coefficient for 2-1 P(8) line.

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Assuming a natural $CH_4$ abundance of 1.6 ppm[9], Table II gives the $CH_4$ absorption coefficients for the three laser lines as extrapolated from the experimental data. For comparison the calculated values[4] are also given.

TABLE II

| | V ($cm^{-1}$) | $K_{exp}^{OSC}$ ($km^{-1}$) | $K_{calc}$ ($km^{-1}$) |
|---|---|---|---|
| 2-1 P(6) | 2680.17 | 15.2 E-4 | 3.103 E-4 |
| 2-1 P(7) | 2655.85 | 11.3 E-4 | 6.015 E-4 |
| 2-1 P(8) | 2631.06 | 8.59 E-4 | 7.884 E-4 |

These measurements will be used to calibrate the spectrophone for the United Aircraft experiments.

V.    SUMMARY

Recent DF laser absorption measurements made with the multi-traversal cell have been presented.

An experiment using a one watt DF laser and an acoustic spectrophone is being planned. With this device we will examine normal sea level air as well as some of the special mixtures which have been studied in the multi-traversal cell.

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[2]  Professor W. S. Benedict, Private Communication, University of Maryland.

[3]  Orlo Myers, Private Communication, General Dynamics, Convair Aerospace Division, San Diego, California.

[4]  F. S. Mills and R. K. Long, "Measured $N_2O$-$N_2$ Absorption at Five DF Laser Frequencies," Report 3271-9, March 1974, The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering; prepared under Contract F30602-72-C-0016 for Rome Air Development Center. (RADC-TR-74-89)

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[8]  Ehhalt and Östlund, Journal of Geophysical Research, Vol. 75, No. 12, April 20, 1970.

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